A COMPARISON OF TWO METHODS FOR DETERMINING THE IONIZATION IN A MIXTURE OF IDEAL GASES AT EQUILIBRIUM

by

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TABLE OF CONTENTS

Page

APPENDICES

LIST OF TABLES

LIST OF SYMBOLS

A, A^+	representative atom or molecule, and ion
B	structure constant, defined in equation (59b)
B_e	spectroscopic constant
B_o	constant, defined in equation (71b)
c	velocity of light
D_e	spectroscopic constant
e	base of natural logarithm
e^-	electron
E	internal energy of an ideal gas
$E^{o'}$	molal internal energy based on common reference level (Appendix B)
f	nondimensional Gibbs free energy, defined in equation (A-2)
F	Gibbs free energy of an ideal gas; function of free energy
F^o	molal standard free energy
$F^{o'}$	molal standard free energy based on common reference level (Appendix B)
g	degeneracy of energy level
G	function of free energy, defined in equation (A-11)
h	Planck's constant
H_o^o	standard heat of formation at 0 ^oK
I	moment of inertia
j	rotation quantum number

k	Boltzmann's constant
K_P	equilibrium constant
m	particle mass; number of components
n	number of species
N	number of particles
N_o	Avagadro's number
P	pressure; constant, defined in equation (71c)
P^o	standard pressure (= 1 atmosphere)
q	constant, defined in equation (71d)
Q	particle partition function; function of free energy, defined in equation (A-10)
Q'	Q/N_o, equation (50); particle partition function based on common reference level (Appendix B)
$\overline{Q}$	grand (or total) partition function
r_i	mols of reactant specie i
R	gas constant
R_i	reactant specie i
s_j	mols of product specie j
S	entropy of an ideal gas
S_j	product specie j
T	temperature
u	constant, defined in equation (71e); also, variable defined in equation (A-18)
v	vibration quantum number
V	volume

x	number of mols
$\bar{x}$	total mol number
X	set of mol numbers
y	number of mols
$\bar{y}$	total mol number
Y	set of mol numbers
α	degree of ionization
α_e	spectroscopic constant
β	number of mols
β_o	constant, defined in equation (71a)
δ_{ij}	Kronecker delta
Δ	mol number difference
$\bar{\Delta}$	total mol number difference
ϵ	energy
ϵ'	energy from common reference level (Appendix B)
ϵ_o	ground state energy
μ	chemical potential
ν	vibration frequency
π	Lagrange multiplier
χ	constant, defined in equation (71f)
χ_e	spectroscopic constant
ω	given by ν/c
ω_e	spectroscopic constant

Subscripts

A	vibrational anharmonicity
elec	electronic
H	harmonic oscillator
i	energy level index; specie index; reactant specie index
int	internal
I	vibration-rotation interaction
IP	ionization potential
j	component index; product specie index; rotation level index
max	maximum value for vibration quantum number
mix	mixture property
n	energy state index; vibration mode index
p	products
rot	rotation
R	reactants; rigid rotator
S	rotational stretching
tr	translational
v	vibration level index
vib	vibration

INTRODUCTION

Within the past few years a great many fluid dynamic problems have arisen in which the temperatures of the gas flow systems rise to extremely high levels. The production of hypersonic flows by plasma devices and reentry of spacecraft into planetary atmospheres are typical examples in which high temperature phenomena occur, to mention only two. Within the fluid flow fields of systems such as these there are numerous chemical reactions taking place. At the higher temperature levels (above six thousand degrees Kelvin) the ionization process is one of the more significant reactions which occurs. In planetary atmospheric reentry, for example, ionization in the flow field results in attenuation of radio signals which may be transmitted either to or from the spacecraft. This phenomenon has been observed in flights of both the Mercury and Gemini programs. In the present thesis two methods for determining ionization are investigated, and a comparison is made between the results obtained from each of the two methods over wide ranges of temperature and pressure.

In fluid flow problems involving high temperatures, the determination of the equilibrium composition of the gas is a necessary part of the problem solution. At low to moderate temperatures, a gaseous mixture such as air is essentially inert. At temperatures of about one thousand degrees Kelvin the mixture becomes chemically reactive and new chemical species are formed in the mixture. Some of these species will be products of the dissociation of diatomic and polyatomic molecules. As temperature increases to several thousand degrees Kelvin dissociation becomes the principle chemical reaction; whereas, at still higher temperatures the ionization process begins to occur.

In problems involving dissociation and ionization, considerable simplification can be obtained by assuming the existence of temperature boundaries. For example, at temperatures below one thousand degrees Kelvin the mixture may be considered to be non-reactive. Below six thousand degrees, on the other hand, while including dissociation reactions, it may be possible to neglect the ionization process. Above six thousand degrees it is assumed that dissociation has been completed and that only ionization remains as the predominant chemical reaction. In the actual physical case such hypothetical temperature boundaries do not exist. Instead, a gradual transition occurs continuously with increasing temperature. The temperature range over which a transition may appear to take place depends upon the particular chemical species in the mixture as well as upon the total pressure of the gas. Both methods for determining ionization, which will be studied in this thesis, may be applied either below, in, or above the transition temperature range. In one of the two methods considered, the ionization process is included as an integral part of the equilibrium composition at all temperatures and pressures. In the second method the ionization of each individual specie within the equilibrium mixture is determined separately. This method proves particularly useful when a discrete temperature boundary is assumed.

One procedure for determining the equilibrium composition of a mixture of gases, the method of steepest descent, is presented in reference 1. In this method an iterative scheme is used to minimize the total Gibbs free energy of the chemical mixture. Within each iteration cycle a system of simultaneous linear equations must be solved, the number of equations being one greater than the number of chemical elements within the mixture. The complexity of the problem depends primarily upon the number of elemental components from which the species of the mixture are formed. When this method is used to determine an equilibrium composition, a large increase in the number of reaction products increases the complexity of the problem only slightly.

Both methods considered in this thesis for determining equilibrium ionization use the procedure of minimizing the free energy of a gaseous mixture. In the equations of minimization in the first method electrons are treated as one of the chemical elements. Neutral species are considered to have no electrons, and positive ions are considered to be formed from the neutral species with a resulting deficiency of electrons. In this fashion the degree of ionization which occurs in the first method may be determined directly.

In the second method the equilibrium composition of the mixture is determined by following the steepest descent procedures of reference 1; but with the important exception that ionization is not included. By excluding ionization, there is one less component of the mixture and the system of simultaneous equations has one less equation. Also, ionization species are not included in the list of reaction products.

After having determined the equilibrium composition in the absence of ionization, the approximate degree of ionization which actually occurred in the mixture can then be found by calculating the ionization of each individual specie using an expression equivalent to the Saha equation given in reference 2. It has been observed that this second method results in a reduction of computing time by about sixty percent over the first method.

For a mixture of one thousand grams of air and ten grams of water vapor, the ionization as determined by the two methods compared favorably over a wide range of temperatures and pressures. The results of this comparison indicate that Saha's equation provides a useful method for approximating the ionization in a mixture of gases, particularly under the following constraints: a computer program not including ionization is available for determining the equilibrium composition of gaseous mixtures, only limited computing facilities are available; available computing time does not permit determination of ionization as an integral part of the equilibrium system.

Chapter One

THE PARTITION FUNCTION IN THERMODYNAMICS

In computing the thermodynamic properties of a gas mixture there are essentially two principal methods presently in use. In the first method heat capacity data is obtained experimentally and the other thermodynamic properties are then derived from the experimental data. A second method which is frequently used for computing the thermodynamic properties of a gas requires the use of molecular data obtained from the spectra of the species of the gas. As noted in reference 3, this latter method frequently gives more accurate values for the thermodynamic properties than the first method.

In numerous references on statistical and physical chemistry (e.g., references 4, 5, and 6), the thermodynamic properties of a gas mixture are obtained in terms of the grand partition function. For a homogeneous gaseous system composed of N identical particles, the grand (or total) partition function $\bar{Q}$ is the sum over the energy states of the system and is given by

$$\bar{Q} = \sum_{n} \exp\left(-\frac{\epsilon_n}{kT}\right) \qquad (1)$$

where ϵ_n is the energy of the n^{th} state, k is Boltzmann's constant, and T is the absolute temperature of the mixture. If desirable, the partition function in equation (1) may be written in terms of energy levels instead of energy states. If the number of energy states having energy ϵ_i is given by g_i, then g_i may be considered as the degeneracy of the ϵ_i energy level, and the partition function in equation (1) becomes

$$\bar{Q} = \sum_i g_i \exp \left(- \frac{\epsilon_i}{kT} \right) \quad . \tag{2}$$

An expression similar to equation (2) may also be obtained for the total partition function of a single molecule. This particle partition function, Q, is related to the total partition function, $\bar{Q}$, of a system of N indistinguishable molecules, by the expression

$$Q = (N! \; \bar{Q})^{1/N} \quad . \tag{3}$$

The energy levels of a molecule may be calculated from data obtained from quantum mechanics and from spectroscopy, in which case the partition function of the molecule then becomes readily suitable for the calculation of thermodynamic functions. The molecular partition function can be expressed as a product of (or as a function of) partition functions for external and internal degrees of freedom of the molecule. The partition functions for the degrees of freedom of the molecule and the molecular partition function are developed in Chapter Four.

In reference 4 the internal energy and entropy of a gas mixture are obtained in terms of the particle partition function, whereas other thermodynamic properties of the mixture are then obtained from combinations of these internal energy and entropy expressions. From the relation between the thermodynamic probability and entropy, the entropy of N particles may be expressed in terms of the internal energy E and the particle partition function. The thermodynamic function needed to determine the equilibrium composition is the Gibbs free energy. As will be shown, the free energy does not depend on the internal energy directly and the expression for the internal energy, E, is not given here. The entropy of N particles is

$$S = \frac{E}{T} + Nk + Nk \ln \left(\frac{Q}{N} \right) \quad . \tag{4}$$

The Gibbs free energy F is given by the relation

$$F = E - TS + pV \quad . \tag{5}$$

For an ideal gas $pV = NkT$, which, when substituted into equation (5), gives

$$F = E - TS + NkT. \tag{6}$$

Substitution of equation (4) into equation (6) then yields

$$F = - NkT \ln \left(\frac{Q}{N} \right) \quad , \tag{7}$$

and as stated above, F does not depend on E.

In reference 5, Moore derives an expression for entropy from the thermodynamic probability and internal energy but also utilizes the third law of thermodynamics and the concept of heat capacity.

His expression for the entropy is

$$S = \frac{E}{T} + k \ln \overline{Q} \quad . \tag{8}$$

Stirling's approximation formula for large factorials is

$$N! = \left(\frac{N}{e} \right)^{N} \tag{9}$$

When equation (9) is combined with equation (3), and then substituted into equation (4), it can be seen that the result reduces to equation (8). This simply demonstrates the equivalence between equations (4) and (8).

A different approach to the development of thermodynamic relations is used in reference 6. The chemical potential per particle, μ, for a system containing N particles is obtained in terms of Q and is given by

$$\mu = kT (\ln N - \ln Q) \quad . \tag{10}$$

The total free energy then becomes

$$F = N\mu = - NkT \ln \left(\frac{Q}{N} \right) \tag{11}$$

which is also seen to be identical to equation (7). From this expression entropy can be obtained using the classical thermodynamic relation

$$S = - \left(\frac{\partial F}{\partial T} \right)_{p} \tag{12}$$

Other thermodynamic functions may be formed from combinations of S and F. For example, the enthalpy H would be given by H = F + TS.

Chapter Two

DETERMINATION OF CHEMICAL EQUILIBRIUM

In determining the equilibrium composition of a mixture of gases, two primary methods are presently in widespread use. While each of these two methods is distinct in its development and application, both are derived from a common principle, namely, the fact that the condition of equilibrium for a gaseous mixture is determined when the Gibbs free energy of that mixture reaches a minimum. In one of these two methods the partial pressures (or the mol numbers) of each specie within the mixture are determined through use of equilibrium constants. In the other method the free energy of the mixture of gases is minimized directly. In theory these two methods are equivalent, since it can be shown that the equilibrium constants may be derived from the condition that the Gibbs free energy is a minimum for a mixture of gases in equilibrium.

Although the state of equilibrium may be reached by an irreversible process, the equilibrium composition can be determined as if the process leading to equilibrium occurred along a reversible path. In reference 7 it is shown that for a reversible process occurring at constant temperature and pressure, the chemical potential is directly related to the Gibbs free energy, and also that at equilibrium the chemical potential (and the Gibbs free energy) is a minimum. Thus, the equilibrium composition of a mixture of gases becomes defined as that composition for which the Gibbs free energy of the mixture is a minimum.

Section A. The Free Energy of a Mixture of Ideal Gases.

For a reversible process, reference 8 gives the expression

$$dF = - S\ dT + V\ dP \quad . \tag{13}$$

For a process at constant temperature, dT = 0, and for one mole of an ideal gas $pV = RT$. With these substitutions, equation (13) then becomes

$$dF = \frac{RT}{P}\ dP = RT\ d\ \ln P \quad . \tag{14}$$

In reference 5, equation (14) is integrated between the standard state for which the free energy is F^o and the pressure is P^o, and a second state with free energy F and pressure P, giving

$$F - F^o = RT\ \ln \frac{P}{P^o} \quad . \tag{15}$$

Equation (15) gives the molal free energy of an ideal gas at pressure P and temperature T in terms of the standard molal free energy, F^o, and the standard pressure P^o. For the standard state the pressure is one atmosphere, in which case equation (15) may be written as

$$F = F^o + RT\ \ln P \tag{16}$$

with pressure expressed in atmospheres.

For a mixture of ideal gases the free energy of the i^{th} specie is

$$F_i = F_i^o + RT \ln P_i \tag{17}$$

where F_i is the molal free energy of the i^{th} specie, F_i^o the standard molal free energy and P_i the partial pressure of the i^{th} specie. Dalton's Law of Partial Pressures gives P_i in terms of x_i (i.e., the number of mols of the i^{th} specie), the total number of mols $\bar{x}$, and the total pressure P as

$$P_i = \frac{x_i}{\bar{x}} P \quad . \tag{18a}$$

With n species in the mixture $\bar{x}$ is given in terms of x_i as

$$\bar{x} = \sum_{i=1}^{n} x_i \quad , \tag{18b}$$

and P in terms of P_i is given by

$$P = \sum_{i=1}^{n} P_i \quad . \tag{18c}$$

Equation (18a) may be substituted into equation (17) giving

$$F_i = F_i^o + RT \ln \left(\frac{x_i}{\bar{x}} P \right) \quad . \tag{19}$$

Since the free energy is an additive property, the free energy of the mixture, F_{mix}, is given by summing equation (19) for the n species, that is,

$$F_{mix} = \sum_{i=1}^{n} x_i F_i \quad . \tag{20}$$

Section B. The Equilibrium Constant.

In a chemical reaction where the chemical formulas of the reactants and products are indicated by R_i and S_j, respectively, and there are r_i and s_j mols of each reactant and product specie, respectively, the equilibrium equation is

$$\sum_i r_i R_i \rightleftharpoons \sum_j s_j S_j \quad . \tag{21}$$

As a specific example of equation (21), for the formation of water the equilibrium equation is

$$2 H_2 + O_2 \rightleftharpoons 2 H_2 O \quad .$$

Associated with equation (21) is the equilibrium constant K_P, an expression for which may be obtained from the Law of Mass Action (see, for example, reference 7). In terms of the equilibrium partial pressures of the reactants and products, P_i and P_j, respectively, the equilibrium constant is given by

$$K_P = \frac{\pi_i \, P_j^{s_j}}{\pi_i \, P_i^{r_i}} \quad . \tag{22}$$

For the example of water given above the equilibrium constant would be

$$K_{P\,H_2O} = \frac{P_{H_2O}^{\,2}}{P_{O_2} \, P_{H_2}^{\,2}} \quad .$$

The equilibrium constant can also be written in terms of the mol numbers by use of Dalton's Law of Partial Pressures. Substituting equation (18a) into equation (22) gives

$$K_P = \frac{\pi_i \, x_j^{s_j}}{\pi_i \, x_i^{r_i}} \; P^{\Sigma s_j - r_i} \; . \qquad (23)$$

Distinct from the equilibrium equation is the reaction equation. Using the symbols previously defined in equation (21), a corresponding reaction equation would be

$$\sum_i r_i R_i \longrightarrow \sum_j s_j S_j \quad . \qquad (24)$$

In a reaction equation, such as equation (24), chemical species which appear on the left side as reactants may also appear on the right side as products. In an equilibrium equation, such as equation (21), the reactant and product species are distinct. Furthermore, there may be (and usually are) many equilibrium equations associated with each reaction equation.

The equilibrium constants may be calculated from the standard molal free energies of the reactant and product species. For the equilibrium expressed by equation (21), the Gibbs free energy of the reactants would be

$$F_R = \sum_i r_i F_i = \sum_i r_i (F_i^{\,o} + RT \ln P_i) \qquad (25)$$

by use of equation (17). For the products the Gibbs free energy is

$$F_P = \sum_j s_j F_j = \sum_j s_j (F_j^o + RT \ln P_j) \quad . \tag{26}$$

Combining equations (25) and (26), and with $\Delta F \equiv F_P - F_R$, there is obtained

$$\Delta F = \sum_j s_j F_j^o - \sum_i r_i F_i^o + \sum_j s_j RT \ln P_j - \sum_i r_i RT \ln P_i \quad . \tag{27}$$

Since equation (27) was formed for the species in an equilibrium reaction, the P_j and P_i are the equilibrium partial pressures of the product and reactant species, respectively. Application of the condition that the Gibbs' free energy must be a minimum for this mixture, at chemical equilibrium, gives $\Delta F = 0$.

Equation (27) can then be written as

$$\sum_j s_j F_j^o - \sum_i r_i F_i^o = RT \left(\sum_i \ln P_i^{r_i} - \sum_j \ln P_j^{s_j} \right) \quad . \tag{28}$$

Defining this expression as ΔF^o, and rearranging the logarithmic terms, equation (28) may be expressed as

$$- \Delta F^o = RT \ln \left(\frac{\pi_j P_j^{s_j}}{\pi_i P_i^{r_i}} \right) \quad . \tag{29}$$

Substitution of equation (22) into equation (29) then gives

$$- \Delta F^o = RT \ln K_P \quad , \tag{30}$$

or, solving for the equilibrium constant

$$K_P = \exp \left(\sum_i r_i F_i^o - \sum_j s_j F_j^o \right) / RT \quad . \qquad (31)$$

By using equation (31) the equilibrium constants for a set of equilibrium reactions may be computed. Then the equilibrium composition for a given reaction can be obtained by solving for the partial pressures or the mol numbers using the equilibrium equations and the equilibrium constants associated with the reaction.

Section C. The Method of Minimization of Free Energy.

When solving for an equilibrium composition using the method of equilibrium constants, as described above, the free energy of the system is implicitly minimized. The equilibrium composition may also be determined by minimizing the Gibbs free energy explicitly. Equations (20), (19), and (18b) give the free energy of a mixture, F_{mix}, as a function of n variables (i.e., the mol numbers x_i) when there are n species in the mixture. The equilibrium composition is given by the set of mol numbers for which F_{mix} is a minimum. Partial differentiation of F_{mix} with respect to the mol numbers would give n equations in the n mol numbers. The mol numbers, however, are not independent, since conservation laws must be obeyed. Mass conservation provides a constraint equation for each kind of atomic nuclei present in the mixture. If ionization is considered, then conservation of charge provides an additional constraint equation. Thus, for m components in the mixture, there are m constraint equations. The fact that the equations are not independent is of less concern than is the fact that the n equations are nonlinear in the mol numbers x_i. In reference 1 a method is presented whereby a linear set of equations is obtained by forming a function which approximates the free energy of the mixture, followed by differentiation of this function. An outline of this method is given in the following discussion; whereas a detailed development of the method, including appropriate equations, is deferred until Appendix A.

Initially, an arbitrary set of positive mol numbers, denoted by $Y = \{y_1, y_2, \ldots, y_n\}$, may be chosen which satisfies the m constraint equations. For this set of mol numbers, the function F(Y) is formed, where F(Y) is a function of the free energy of the mixture. The procedure for determining the equilibrium composition then begins by expanding F(Y) in a Taylor's series in the neighborhood of Y. Neglecting terms in the expansion higher than second order gives Q(X), a function of the free energy which is a quadratic approximation to F(Y), where X is a set of mol numbers in the neighborhood of Y. Before minimizing Q(X), the constraint equations and Q(X) are combined, with the introduction of Lagrange multipliers, to give a second function G(X). Partial differentiation of G(X) with respect to the mol numbers x_i then yields n linear equations in the mol numbers, the Lagrange multipliers, and the total mol number, $\bar{x}$.

These equations, together with the constraint equations and equation (18b), give a system of n + m + 1 linear equations in n + m + 1 unknowns. By substitution and summation, the system is reduced to m + 1 linear, independent equations in m + 1 unknowns. Solution of these equations permits determination of the set of mol numbers x_i which minimizes Q(X). This set of mol numbers gives a value of the free energy function F less than the value of F(Y) but does not minimize F since Q(X) is only an approximation to F(Y). The set Y may be replaced by the set X and the above procedure repeated until the sequence of sets of mol numbers converges to the desired degree.

In this method, before each new iteration cycle is begun, two tests are made on the new set of mol numbers X. First, a check is made to determine if the minimum point of F has been passed. If so, the mol numbers are adjusted so that the minimum of F will not be passed. The details of how this is accomplished are presented in Appendix A. In theory, the mol numbers X obey the constraint equations, since the constraints are included in the system of equations to be solved. Since a large number of arithmetic operations occur in the solution of the equations, however, significant round off errors can accumulate. The second test of the mol numbers determines the extent of these round off errors. The mol numbers are then adjusted to compensate for round off errors so that the constraint equations are obeyed in fact.

The above method for determining the equilibrium composition of a mixture of ideal gases is compared with two other methods in reference 9. It is shown that this method is equivalent to the methods of Huff and Brinkley. It is also shown that the method of reference 1 converges.

Chapter Three

THE IDEAL IONIZING GAS

In determining the amount which a single specie gas would ionize, a procedure such as outlined in section C of Chapter Two could be used. However, for a single chemical reaction the answer is obtained more directly by using the equilibrium constant for the reaction.

For an ideal gas, designated by the letter A, the reaction equation is

$$YA \longrightarrow \beta_A A + \beta_{A^+} A^+ + \beta_{e^-} e^- \qquad (32)$$

In this equation Y is the number of mols of A before ionization is considered, β_A is the number of mols of A after ionization is taken into account, β_{A^+} and β_{e^-} are respectively the number of mols of the ion of A and electrons produced by ionization.

For a monatomic gas at high temperatures ionization would be the only reaction to be expected. For a diatomic or a polyatomic gas, normally dissociation is considered to take place before there is any ionization. However, there is not a sharp boundary between dissociation and ionization, and there will be some ionization of a diatomic specie before the specie is completely dissociated. This would be particularly true for a specie which has a strong chemical bond but which has an outer electron that may be easily removed.

(An example of such a specie is NO.) If the dissociation of the diatomic or polyatomic gas has been determined by other means (without considering any ionization) and Y mols of the specie remain which were not dissociated, then equation (32) could be used to determine the amount of ionization, if any, of the undissociated specie. Further discussion of the use of equation (32) for diatomic species is given in Chapter Five.

Under the assumption that dissociation has been treated separately, the reaction equation (32) is quite general and may be considered to represent the ionization of polyatomic and diatomic as well as monatomic species.

The number of particles of each specie involved in equation (32) is given by multiplying the number of mols, β, by Avagadro's number; thus

$$N_A = N_o \beta_A \tag{33a}$$

$$N_{A^+} = N_o \beta_{A^+} \tag{33b}$$

$$N_{e^-} = N_o \beta_{e^-} \quad . \tag{33c}$$

Conservation of mass requires that there be no change in the number of atomic nuclei due to ionization, so that

$$Y = \beta_A + \beta_{A^+} = \frac{N_A + N_{A^+}}{N_o} \quad , \tag{34a}$$

and conservation of electron charge requires that

$$N_{A^+} = N_{e^-} \quad . \qquad (34b)$$

For the reaction (32) a measure of the extent of ionization is given by the so-called degree of ionization, α, which denotes the fraction of specie A that has been ionized. Therefore, the difference $1 - \alpha$ gives the fraction of specie A that has not been ionized. By its definition α may be expressed as

$$\alpha = \frac{B_{A^+}}{Y} = \frac{B_{A^+}}{B_A + B_{A^+}} \quad , \qquad (35a)$$

or, in terms of the number of molecules, α is given by

$$\alpha = \frac{N_{A^+}}{N_A + N_{A^+}} \quad . \qquad (35b)$$

There is only one equilibrium equation associated with the reaction in equation (32). The equilibrium equation is

$$A \rightleftharpoons A^+ + e^- \quad . \qquad (36)$$

From Chapter Two, the equilibrium constant for this reaction would be given by

$$K_P = \frac{P_{A^+} P_{e^-}}{P_A} \qquad (37)$$

where P_{A^+}, P_{e^-} and P_A are the partial pressures of A^+, e^-, and A respectively.

The pressure of an ideal gas with n mols or N particles is given by

$$PV = nRT = NkT \quad . \tag{38a}$$

In a mixture of ideal gases, the partial pressure of each specie depends on the number of particles of that species present in the mixture. For specie i the partial pressure is given by

$$P_i V = N_i\, kT \quad . \tag{38b}$$

By Dalton's law of partial pressures the total pressure of the mixture is the sum of the partial pressures; that is

$$P = \sum_i P_i \quad . \tag{39}$$

Now the partial pressures for the species in the reaction of equation (32) are given by the expressions

$$P_A = N_A \frac{kT}{V} \tag{40a}$$

$$P_{A^+} = N_{A^+} \frac{kT}{V} \tag{40b}$$

$$P_{e^-} = P_{A^+} = N_{e^-} \frac{kT}{V} \tag{40c}$$

and the total pressure will be given by

$$P = P_A + 2\, P_{A^+}$$

or

$$P = (N_A + 2\, N_{A^+}) \frac{kT}{V} \quad . \tag{41}$$

Thus, substitution of equations (40) into equation (37) gives an equilibrium constant in terms of the number of molecules as

$$K_P = \frac{N_{A^+}^{\;2}}{N_A} \frac{kT}{V} \quad . \qquad (42a)$$

Using equation (41) to eliminate V in this expression there will be obtained the result

$$K_P = \frac{(N_{A^+})^2}{N_A(N_A + 2\,N_{A^+})} P \quad . \qquad (42b)$$

By rearranging equation (35b), N_{A^+} can be given in terms of N_A and α as

$$N_{A^+} = \frac{\alpha}{1 - \alpha} N_A \qquad (43)$$

Substituting equation (43) into equation (42b) gives the equilibrium constant as a function of α and P, namely

$$K_P = \frac{\alpha^2}{1 - \alpha^2} P \quad . \qquad (44)$$

From this equation it can be seen that the degree of ionization may now be computed from the equilibrium constant by simply rearranging equation (44) to yield

$$\alpha = \sqrt{\frac{K_P}{K_P + P}} \quad . \qquad (45)$$

In the above equations, as in the equations of Chapter Two, the pressure should be expressed in atmospheres, whereas the equilibrium constant is dimensionless.

As in the preceding chapter, the equilibrium constant may also be obtained from the standard molal free energy of each specie. From equation (31), the equilibrium constant for the ionization expressed by reaction (32) will be given by

$$K_P = \exp\left[\frac{F^o}{RT})_A - \frac{F^o}{RT})_{A^+} - \frac{F^o}{RT})_{e^-}\right] . \qquad (46)$$

The calculational procedure for determining mol numbers then would be as follows: determine the equilibrium constant from equation (46); determine the degree of ionization from equation (45); and then calculate the mols of each specie using equations (35a), (34a) and (34b).

In the following chapters, reference will be made to the method of Saha and to Saha's equation. Equation (44), above, and thus also equation (45), are equivalent to the equation of Saha. Combining equations (44) and (46) gives

$$\frac{\alpha^2}{1-\alpha^2} = \frac{1}{P} \exp\left[\frac{F_A{}^o}{RT} - \frac{F_{A^+}{}^o}{RT} - \frac{F_{e^-}{}^o}{RT}\right] . \qquad (47)$$

In Chapter One the standard molal free energy was given in terms of the particle partition function. In order to use the free energies calculated from these equations, the energy levels of the particles must be given from a common reference level. Appendix B gives a procedure which permits calculation of the particle partition function using the energy levels of the particle. The energy levels are then referred to a common reference level by adding one term to the expression for the Gibbs free energy. As given by Equation (B-8), the standard molal free energy then can be expressed as

$$\frac{F^o}{RT} = \frac{H_o^{\;o}}{RT} - \ln \left(\frac{Q}{N_o} \right) . \tag{48}$$

Substitution of equation (48) into equation (47) gives

$$\frac{\alpha^2}{1-\alpha^2} = \frac{1}{P} \exp \left[\left.\frac{H_o^{\;o}}{RT}\right)_A - \ln \frac{Q_A}{N_o} - \left.\frac{H_o^{\;o}}{RT}\right)_{A^+} + \ln \frac{Q_{A^+}}{N_o} - \left.\frac{H_o^{\;o}}{RT}\right)_{e^-} + \ln \frac{Q_{e^-}}{N_o} \right] . \tag{49}$$

Designating the partition function divided by Avagadro's number as Q' and collecting terms gives

$$\frac{\alpha^2}{1-\alpha^2} = \frac{1}{P} \frac{Q_{A^+}{}' \, Q_{e^-}{}'}{Q_A{}'} \exp \left[\frac{\left.H_o^{\;o}\right)_A - \left.H_o^{\;o}\right)_{A^+} - \left.H_o^{\;o}\right)_{e^-}}{RT} \right] . \tag{50}$$

In the above equation $\left.H_o^{\;o}\right)_{e^-}$ is zero and $\left.H_o^{\;o}\right)_A$ differs from $\left.H_o^{\;o}\right)_{A^+}$ by the ionization potential in ergs/mol multiplied by Avagadro's number; that is,

$$\left.H_o^{\;o}\right)_A - \left.H_o^{\;o}\right)_{A^+} = - N_o \, \epsilon_{IP} , \tag{51}$$

where ϵ_{IP} is the ionization potential. With equation (51) and the relation $R = N_o k$, equation (50) may be written in the following form:

$$\frac{\alpha^2}{1 - \alpha^2} = \frac{1}{P} \frac{Q_{A^+}{}' \, Q_{e^-}{}'}{Q_A{}'} \exp\left(- \frac{\epsilon_{IP}}{kT} \right) . \qquad (52)$$

Equation (52) is one form of Saha's equation. In the next chapter the partition function expressions for several types of particles are developed. By expanding the partition functions in equation (52) in terms of such expressions, this Saha relationship may be rewritten in its more conventional form.

In some applications it proves desirable to compute α from equation (52) or from alternative forms which are equivalent to (52). In the present work, however, since the standard molal free energies are needed in the computation of equilibrium compositions utilizing the method of free energy minimization, it is most convenient to determine α from equations (45) and (46).

Chapter Four

THE PARTITION FUNCTION OF A PARTICLE

The thermodynamic functions of an ideal gas may be computed either from the partition function of the gas or from the partition function of the particles composing the gas. Since the energy levels and the degeneracies are either tabulated or are derived on a per-particle basis, the particle partition function is more direct and more convenient to use.

With the energy of the i^{th} energy level given by ϵ_i and the degeneracy given by g_i, the partition function of the particle is

$$Q = \sum_i g_i \exp\left(-\frac{\epsilon_i}{kT}\right) \quad . \tag{53}$$

For any energy state of the particle, the energy may be thought of as being comprised of two components. One component of the total particle energy is the energy due to translational motion. The other component of the energy is the internal energy due to electron excitation and, in the case of diatomic and polyatomic molecules, also including the rotational and vibrational contributions. These two components of the energy are independent of each other and are therefore separable. Also, at any level of total energy, the degeneracy of that level is the product of the translational degeneracy and the internal degeneracy. Using the subscripts tr for translational and int for internal, equation (53) may be written as

$$Q = \sum_i (g_{tr})_i \, (g_{int})_i \exp\left[- \frac{(\epsilon_{tr})_i}{kT} - \frac{(\epsilon_{int})_i}{kT} \right] . \qquad (54)$$

Thus the partition function Q is the product of a translational partition function and a partition function due to internal energy levels. Equation (54) may then be written

$$Q = Q_{tr} \quad Q_{int} \qquad (55a)$$

where Q_{tr} is given by

$$Q_{tr} = \sum_i (g_{tr})_i \exp\left[- \frac{(\epsilon_{tr})_i}{kT} \right] \qquad (55b)$$

and Q_{int} is given by

$$Q_{int} = \sum_i (g_{int})_i \exp\left[- \frac{(\epsilon_{int})_i}{kT} \right] . \qquad (55c)$$

Section A. The Translational Partition Function.

The energy levels of a particle due to its translational motion are derived in most texts on quantum mechanics (e.g., reference 6). These energy levels are obtained from the Schrodinger wave equation where it is assumed that the particle is confined within a cube of volume V, the impact of the particle against the walls of this container is treated as a perfectly elastic reflection, and the particle is assumed free of interactions with any other particles. The energy levels so derived are very closely spaced and, when substituted into equation (55b), the resulting infinite series may be replaced by an integral expression. In reference 6 this procedure is used to determine Q_{tr}. Evaluation of the integral gives the result

$$Q_{tr} = \left(\frac{2\pi \; m \; kT}{h^2} \right)^{3/2} V \; , \tag{56}$$

where m is the mass of the particle and h is Planck's constant. For an ideal gas comprised of N particles the relation $PV = NkT$ holds true, and equation (56) may then be written as

$$Q_{tr} = \left(\frac{2\pi \; m \; kT}{h^2} \right)^{3/2} \frac{NkT}{P} \; . \tag{57}$$

Equation (57) can be used to calculate the molal standard free energy from the partition function, since for one mole of gas in the standard reference state the number of particles would be given by Avagadro's number and the pressure would be one atmosphere.

Section B. The Internal Partition Function.

The internal energy of a molecule may be due to contributions from several sources. For a diatomic molecule the internal energy will, in general, be composed of contributions from rotation, vibration, nuclear energy, and energy from electron excitation. For chemical reactions in which the atomic nuclei are conserved, the terms contributed to the partition function by the nuclear energy are the same for both the reactants and the products. These terms cancel out and are not considered in calculating the thermodynamic functions for ordinary chemical reactions.

For atomic species the only contribution to the internal energy is that from electron excitation, and the internal partition function in this case reduces to

$$Q_{int} = \sum_{i} g_i \exp\left[-\frac{(\epsilon_{elec})_i}{kT}\right] . \tag{58}$$

Equation (58) is an infinite series and, in theory, all terms should be considered in evaluating Q_{int}. In practice, however, only a finite number of terms can be included and, in fact, need to be included. For the atomic species, only a portion of the theoretically possible energy levels are tabulated. Even then, except at extremely high temperatures, it is not necessary to use all of the energy levels which are available, since the series in equation (58) can be terminated at that point where the exponential terms become negligibly small compared to the ground state term. The first term of the series, that for the ground state, has a value of one or larger, whereas subsequent terms may have values less than 10^{-6}, which may be considered negligible.

For a diatomic molecule the contributions to the internal energy come from the rotation of the molecule, vibration, and excitation of electrons. An approximation of the internal energy of the molecule is obtained by making several simplifying assumptions which are valid at low and moderate temperatures.

First, it is assumed that excitation of electronic states above the ground state do not affect the rotational and vibrational motion of the molecule. Unless there is an electronic state with energy quite close to the ground state, the excited electronic states may be omitted. For a low energy electronic state, the effect on rotation and vibration is slight and the electronic energy terms may be separated from the other contributions to the internal energy. The electronic partition function would then be given by equation (58) with only the first one or two terms retained.

The internal energy of the molecule contributed by rotation is obtained by again solving the Schrodinger wave equation, but with the molecular model this time simulated by a rigid rotator. The molecule is represented as two point masses separated by the internuclear distance which remains constant. The energy levels given by solution of the wave equation under these assumptions are

$$\epsilon_{rot} = j(j + 1) \frac{h^2}{8\pi^2 I} \tag{59a}$$

where j is the rotation quantum number and I is the moment of inertia.

The moment of inertia is often included in a constant, B, which is derived from the spectra of the molecule and is given by

$$B = \frac{h}{8\pi^2 cI} \quad . \tag{59b}$$

Combining equations (59a) and (59b) gives

$$\epsilon_{rot} = j(j + 1)\ h\ c\ B \quad . \tag{59c}$$

For each rotational energy level the degeneracy is 2j + 1.

With the assumptions above, the rotational energy may be treated as independent of the other contributions to the internal energy, and a separate rotational partition function can be formed. Since the energy levels are closely spaced, the infinite series is again replaced by an integral expression. Evaluation of the integral gives the partition function of a rigid rotator as

$$Q_{rot} = \frac{kT}{hcB} \quad . \tag{60}$$

In order to obtain the vibrational energy levels of the molecule, it is assumed that the vibration of the molecule is that of a simple harmonic oscillator. The wave equation then gives the energy levels of such a harmonic oscillator as

$$\epsilon_{vib} = h\nu\ (v + \frac{1}{2}) \tag{61a}$$

where v is the vibrational quantum number and ν is the frequency of vibration, with the degeneracy of each vibrational level being taken as unity. The vibrational frequency is normally tabulated in terms of ω, which is ν/c. The energy of the lowest vibrational level is not zero but rather is 1/2 $hc\omega$. In keeping with the practice of assigning a value of zero to the ground state energy of the molecule, the vibrational energy with $v = 0$ is included in the energy of formation of the molecule and not in the energy of the vibrational levels. The vibrational energy is thus given as

$$\epsilon_{vib} = hc\ \omega v \quad . \tag{61b}$$

The partition function of the harmonic oscillator is then

$$Q_{vib} = 1 + \exp\left(- \frac{hc\omega}{kT} \right) + \exp\left(- \frac{2hc\omega}{kT} \right) + \ldots.. \quad . \tag{62}$$

This infinite series may be rewritten as

$$Q_{vib} = \frac{1}{1 - \exp\left(- \frac{hc\omega}{kT} \right)} \quad . \tag{63}$$

As a result of the above approximations the internal partition function of a diatomic molecule is

$$Q_{int} = Q_{rot}\ Q_{vib}\ Q_{elec} \quad . \tag{64}$$

The assumptions which lead to equation (64) describe the behavior of a diatomic molecule quite well at low and moderate temperatures.

Equations (60), (63), and (64) may be used for calculating thermodynamic functions for temperatures less than about 3000 ^{o}K with very small error. These equations together with the correction terms developed in reference 6 are the basis for the thermodynamic data compiled in reference 10 for temperatures up to 6000^{o} Kelvin.

A review of the assumptions given above shows that at higher temperatures where dissociation and ionization become important effects in a mixture of ideal gases, the behavior of the diatomic molecule should be more accurately represented. For the rotational energy it was assumed that the internuclear distance was constant and thus the moment of inertia of the molecule was constant. At high rotational energy levels the centrifugal force may stretch the molecule and thus alter the moment of inertia. The moment of inertia of the molecule may also be affected by the vibration of the molecule when the higher vibrational levels are excited.

For a harmonic oscillator, a displacement from the equilibrium position gives a restoring force proportional to the displacement. At high vibration levels this force may differ from Hooke's law and the vibrations then become anharmonic. From this discussion it can be seen that the internuclear distance, rather than remaining constant as previously assumed, may be altered considerably by centrifugal stretching.

Excitation of electrons to levels above the ground level may alter the coulomb field surrounding the molecule. A change in the coulomb field would affect both the internuclear force and distance. Thus the rotational and vibrational motion of the molecule would be different for different electronic states of the molecule. In reference 11, for example, the spectroscopic constants describing the structure and the vibration of the molecule are different for the different electronic states of most molecules. When electronic energy levels are quite close together, the spectroscopic constants may be the same.

The representation of the behavior of a diatomic molecule may be improved by determining the energy of vibration and rotation at each electronic energy level. Also, correction terms for anharmonicity, vibration-rotation interaction, and rotational stretching may be added to the energy terms for the rigid rotator and the simple harmonic oscillator. For each electronic energy level, the energy of rotation and vibration is given by

$$\epsilon_{rot,vib} = \epsilon_H + \epsilon_R + \epsilon_A + \epsilon_I + \epsilon_S \quad . \tag{65}$$

In equation (65) the first two terms are the energies of the harmonic oscillator and the rigid rotator, whereas the last three terms are correction terms for anharmonicity, vibration-rotation interaction and rotational stretching.

For a given electronic energy level with vibration quantum number v and rotation quantum number j, the degeneracy is 2j + 1 and the energy of vibration and rotation combined is given by reference 6 as

$$\epsilon_{v,j} = hc\left[(v + \frac{1}{2})\,\omega_e + j(j + 1)\,B_e - (v + \frac{1}{2})^2\,\chi_2\,\omega_e - \right.$$

$$\left. (v + \frac{1}{2})\,j(j + 1)\alpha_e - j^2(j + 1)^2\,D_e\right] \qquad (66)$$

where ω_e, B_e, χ_e, α_e, and D_e are constants derived from the molecular spectra. In equation (66) the terms correspond to the terms in equation (65). If tabulated values of D_e and α_e are unavailable they may be obtained from the theoretical relations

$$D_e = 4\,\frac{B_e^3}{\omega_e^2} \qquad (67a)$$

and

$$\alpha_e = 6\,\frac{B_e^2}{\omega_e}\left[\left(\frac{\omega_e\chi_e}{B_e}\right)^{1/2} - 1\right] . \qquad (67b)$$

The energy given by equation (66) is not zero for v and j equal to zero. As for the simple harmonic oscillator, this energy is included with the energy of formation, not with the energy of vibration and rotation. Denoting this ground state energy by ϵ_o, the energy of vibration and rotation becomes

$$\frac{\epsilon_{v,j} - \epsilon_o}{hc} = v\,\omega_e - (v^2 + v)\,\chi_e\omega_e + j(j + 1)(B_e - \frac{1}{2}\,\alpha_e)$$

$$- j^2(j + 1)^2\,D_e - vj(j + 1)\,\alpha_e \quad . \qquad (68)$$

Using the energy levels in equation (68), the rotation-vibration partition function for each electronic energy level is

$$Q_{vib,rot} = \frac{1}{\sigma} \sum_{v=o}^{\infty} \sum_{j=o}^{\infty} (2j + 1) \exp\left\{- \frac{hc}{kT} \left[v\ \omega_e - (v^2 + v)\ \omega_e \chi_e \right.\right.$$

$$\left.\left. + j(j + 1)(B_e - \frac{1}{2} \alpha_e - j(j + 1)\ D_e - v\ \alpha_e) \right] \right\} . \qquad (69)$$

The summation in equation (69) has been divided by the symmetry number σ. The symmetry number is the number of indistinguishable positions that the molecule may have due to a simple rotation. For a homonuclear diatomic molecule, both atoms of the molecule are the same, and the symmetry number then will be two. For a molecule of two different atoms, a heteronuclear diatomic molecule, the symmetry number is unity. From quantum mechanics, all rotational quantum numbers are not allowed for all molecules. For a homonuclear molecule only even or only odd rotational quantum numbers are allowed. The energy levels are closely spaced and the use of only even or only odd values of j is equivalent to using all values of j in the partition function and dividing the result by two. For a heteronuclear molecule both even and odd values of j are allowed and σ is one.

The series in equation (69) is non-convergent since for large quantum numbers the terms in v^2, j^4 and vj^2 become predominant and cause the argument of the exponential to become positive. This problem arises from the inclusion of the last three terms in equation (66) which are properly correction terms and thus are not valid for extremely large quantum numbers. A finite value for $Q_{vib,rot}$ may be obtained by terminating the summations at some point. If the termination point is properly chosen the value of $Q_{vib,rot}$ will be quite accurate. The energy of the molecule from vibration and rotation given by equation (66) should not exceed the dissociation energy. The only quantum numbers which should be allowed in equation (69) are those which give an energy of vibration and rotation less than the dissociation energy. A maximum value of the vibrational quantum number, v_{max}, is determined which will not permit the energy of a harmonic oscillator to exceed the dissociation energy. Then for each value of v less than v_{max}, all values of j are permitted for which the combined energy of rotation and vibration do not exceed the dissociation energy.

While $Q_{vib,rot}$ may be evaluated by a direct summation of equation (69), considerable computational time and effort can be saved by obtaining compact forms for the series expressions in equation (69). In reference 6 compact forms are derived for both the summation over j and v. High temperature correction terms are developed which are added to the partition functions of rotation and vibration given in equations (60) and (63). The results obtained by this development would be suitable for hand computation, but when an electronic computer is available some of the approximations made in reference 6 need not be included.

By using the Euler-Maclaurin summation formula, a compact expression may be obtained to replace the summation over the rotational quantum number. The vibration-rotation partition function for each electronic energy level which results from this approach is then given by

$$Q_{vib,rot} = \frac{1}{\sigma} \sum_{v=o}^{v_{max}} \left[\frac{1}{\beta_o(1-vq)} + \frac{2P}{\beta_o^2(1-vq)^3} + \frac{1}{3} + \frac{\beta_o(1-vq)}{12} \right] \exp\,(-vu + v(v-1)\ \chi\ u) \tag{70}$$

where

$$\beta_o = \frac{hc}{kT} B_o \tag{71a}$$

$$B_o = B_e - \frac{1}{2} \alpha_e \tag{71b}$$

$$P = \frac{D_e}{B_o} \tag{71c}$$

$$q = \frac{\alpha_e}{B_o} \tag{71d}$$

$$u = \frac{hc}{kT} (\omega_e - 2\ \omega_e\ \chi_e) \tag{71e}$$

and

$$\chi = \frac{\omega_e\ \chi_e}{\omega_e - 2\ \omega_e\ \chi_e} \quad . \tag{71f}$$

With the vibration-rotation partition function given by equation (70), the internal partition function for a diatomic molecule is then given by

$$Q_{int} = \sum_{i} (g_{elec})_i \exp\left[- \frac{(\epsilon_{elec})_i}{kT}\right]\left[Q_{vib,rot}\right]_i \; . \qquad (72)$$

The method of determining v_{max} is given in Appendix C and the derivation of equation (70) using the Euler-Maclaurin summation formula is given in Appendix D.

For polyatomic molecules the extent of the tabulated data frequently permits only the use of the rigid rotator-harmonic oscillator model of the molecule. For a linear, triatomic molecule, such as CO_2, the rotational partition function is the same as equation (60). There are four vibrational modes for a linear, triatomic molecule and the vibrational partition function is the product of the four separate modes. If only the lowest electronic energy level with degeneracy g is considered, the internal partition function of a linear, triatomic molecule will be

$$Q_{int} = \frac{g}{\sigma} \cdot \frac{kT}{hc\, B_o} \prod_{n=1}^{4} \frac{1}{1 - \exp\left(- \frac{hc}{kT}\, \omega_n\right)} \; . \qquad (73)$$

Chapter Five

PROCEDURE AND DISCUSSION OF RESULTS

From the equations of Chapters One and Four, the molal standard free energy was computed using the constants and other data tabulated in Appendices E and F. All species for which the free energy was computed are listed in Table II. The free energy calculations were made for temperatures from 2500 °K to 15,000 °K at intervals of 500 °K. The free energy data for the atomic species was compared with the data given in reference 12 and the agreement found to be within 0.1 percent or better. For the diatomic species and for CO_2 the data was compared with data presented in references 13, 14, and 15. Here again the level of agreement was the same as for the atomic species.

For a mixture composed of 1000 grams of dry air with 10 grams of water vapor added, the equilibrium composition was determined by two methods at eight different temperatures with three pressures considered at each temperature. The range of temperatures was 3000 °K to 10,000 °K in 1000° intervals whereas the pressures used were 0.01 atmosphere, 1.0 atmosphere and 10 atmospheres.[1]

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[1] It was originally intended to compare the results of the two methods over a temperature range of 2500 °K to 15,000 °K in 500° intervals. Funding for the computer usage which would have been required for this range of temperatures was not available and thus the number of temperatures considered was reduced.

In the first method, which will be referred to as the exact method, the equilibrium composition was determined by minimizing the free energy of the mixture of gases by the procedure of reference 1. Ionic species were considered and electrons were treated as a component of the mixture along with hydrogen, carbon, nitrogen, oxygen and argon.

In the second method, which will be referred to as the approximate method, the equilibrium composition was determined in two steps. The first step consisted of calculating the equilibrium composition, again, by the procedure of reference 1, with no ionic species or electrons included in the mixture. In the second step, ten of the species[2] were tested for amount of ionization using Saha's equation. The mol numbers given by step one correspond to the initial number of mols, or Y, required in the relations of Chapter Three. Saha's equation gives the number of mols of the original specie remaining after ionization, the number of mols of the specie ion and the number of mols of electrons from the ionization of the specie. The sum of the number of mols of electrons given by the ionization of the ten species is considered to correspond to the number of mols of electrons given by the exact method.

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[2] For the other four species, H_2, C_2, CN, and CO_2, spectroscopic data was not available for their ions and so the ions of these four species were not included in determining the equilibrium composition by either the exact or the approximate method.

The number of mols of electrons is the principal basis of comparing the results of the two methods. This data is presented in Table I for the eight temperatures and three pressures considered. It is seen from the data that the results of the exact and approximate methods agree almost exactly at the higher temperatures. At the lower temperatures the results differ by a factor of about five or six. The exact method gives a total number of mols in the mixture between 35.8 at 3000 °K and 10 atmospheres pressure and 87.0 at 10,000 °K and 0.01 atmosphere. While the difference in the number of mols of electrons given by the two methods is considerably larger at the lower temperatures than at the higher temperatures, the actual number of mols of electrons contained within the total mixture at these lower temperatures is only a few parts per million.

As samples of the equilibrium compositions given by the two methods, Table II presents the results for P = 0.01 atmosphere and temperatures of 4000 °K and 8000 °K. From this data it is seen that there is good general agreement, especially for the major species. From the data presented in Table I it was seen that the approximate method consistently gave a lower number of electrons than did the exact method, the extent of this underprediction increasing with decreasing temperature. Examination of the data given in Table II for 4000 °K gives some indication of the reason for this discrepancy. The results of the exact method show that the number of mols of NO^+ and the number of mols of electrons are very nearly equal, whereas

T(^{o}K)	P = 0.01 atm		P = 1.0 atm		P = 10 atms	
	Exact	Approximate	Exact	Approximate	Exact	Approximate
3000	6.8895 -06	9.8034 -07	8.4889 -07	1.7914 -07	2.2749 -07	5.9302 -08
4000	4.4517 -04	3.8467 -05	1.2073 -04	2.4264 -05	4.7231 -05	1.2983 -05
5000	5.1597 -03	1.0659 -03	1.5862 -03	2.6361 -04	8.1153 -04	1.8958 -04
6000	3.7787 -02	3.1327 -02	8.6261 -03	2.3406 -03	4.6536 -03	1.1410 -03
7000	3.0975 -01	3.0602 -01	3.4516 -02	2.2849 -02	1.6554 -02	6.6263 -03
8000	1.6075	1.6007	1.5697 -01	1.4826 -01	5.2175 -02	3.7914 -02
9000	5.8516	5.8310	5.8327 -01	5.7609 -01	1.7708 -01	1.6533 -01
10,000	16.226	16.226	1.6738	1.6620	5.1985 -01	5.1004 -01

Note: 6.8895 -06 means 6.8895 x 10^{-6}

TABLE I. Mols of Electrons given by the Exact and Approximate Methods

	T = 4000 ^oK		T = 8000 ^oK	
Specie	Exact	Approximate	Exact	Approximate
e^-	4.4517 -04	3.8467 -05	1.6075 +00	1.6007 +00
H	1.1087 +00	1.1087 +00	1.0622 +00	1.0755 +00
H^+	5.2478 -08	7.7551 -07	4.8775 -02	3.5478 -02
C	3.6190 -07	3.6173 -07	4.1119 -03	6.4894 -03
C^+	9.6995 -12	6.0209 -12	3.3848 -03	1.0046 -03
C^{++}	0.0	---	4.1989 -12	---
N	6.0583 -01	6.0583 -01	5.4322 +01	5.4350 +01
N^+	3.9229 -09	1.5674 -07	1.3198 +00	1.2926 +00
N^{++}	0.0	---	3.2005 -12	---
O	1.3429 +01	1.3430 +01	1.3429 +01	1.3395 +01
O^+	2.5686 -07	5.9715 -06	2.3074 -01	2.6696 -01
O^{++}	0.0	---	5.9922 -16	---
A	2.3360 -01	2.3360 -01	2.3104 -01	2.2993 -01
A^+	1.0877 -10	1.6206 -08	2.5613 -03	3.6668 -03
A^{++}	0.0	---	2.6602 -13	---
H2	1.1283 -04	1.1284 -04	5.7042 -08	6.3821 -08
C2	8.0868 -16	8.0797 -16	4.9211 -12	1.6718 -11
$N2^+$	9.8150 -09	1.6695 -06	4.2152 -04	7.2161 -04
O2	1.5204 -02	1.5205 -02	3.4491 -06	3.3265 -06
$O2^+$	6.1701 -08	9.8502 -08	1.2338 -06	3.2427 -07
$O2^-$	8.0258 -11	---	1.7007 -12	---
OH	2.0641 -03	2.0641 -03	1.1392 -06	1.1965 -06
OH^+	1.1130 -10	1.5411 -09	6.2215 -08	4.3169 -08
CO	7.4960 -03	7.4929 -03	2.6287 -06	4.8142 -06
CO^+	2.0431 -10	3.9771 -09	1.3851 -07	1.7050 -07
NO	1.9278 -01	1.9276 -01	4.4315 -04	3.3524 -04
NO^+	4.4481 -04	2.9773 -05	1.8319 -03	1.3700 -04
CN	6.3432 -08	6.3404 -08	5.1138 -07	9.7628 -07
CO2	2.7291 -06	2.7280 -06	2.0045 -13	3.9548 -13

Note the number of mols of C^{++}, N^{++}, O^{++}, A^{++}, and $O2^-$ were not calculated by the approximate method.

TABLE II. Comparison of Equilibrium Compositions at
P = 0.01 atmosphere and T = 4000 ^oK
and 8000 ^oK

from the approximate method the number of mols of NO^+ present is only about 75 percent of the total number of mols of electrons. Similar situations exist at the lower temperatures where the results of the exact and approximate methods show considerable relative differences in the number of mols of electrons.

Table III gives the number of mols of NO and NO^+ given by the exact method, the number of mols of NO given by step one of the approximate method, and the number of mols of NO and NO^+ given by step two of the approximate method. (Step one and step two of the approximate method are described earlier in this chapter.) From the data in Table III it is seen that step one of the approximate method gives nearly the same number of mols of NO as does the exact method. Also, the ratio of NO^+ to NO is consistently lower by the approximate method than by the exact method.

It is not simply due to the use of Saha's equation that the second method of approach is classified as an approximate procedure. As discussed in Chapter Two, the method of minimizing the free energy of a mixture of gases is equivalent to using equilibrium constants for the determination of its equilibrium composition. In reference 9 it is shown that the procedure of reference 1 is equivalent to a procedure which uses an equilibrium constant formulation. Thus, Saha's equation is exact for a mixture comprised only of a single specie, its ion, and electrons. Such a mixture might be NO, NO^+, and e^-. Using the exact method, the equilibrium composition of this

P = 0.01 atm

Exact Method			Approximate Method		
			Step One	Step Two	
T(°K)	NO	NO$^+$	NO	NO	NO$^+$
3000	7.813 -01	6.912 -06	7.813 -01	7.813 -01	9.543 -07
4000	1.928 -01	4.448 -04	1.928 -01	1.928 -01	2.977 -05
5000	5.894 -02	4.952 -03	5.896 -02	5.879 -02	1.767 -04
6000	1.243 -02	1.093 -02	1.246 -02	1.218 -02	2.810 -04
7000	2.020 -03	4.444 -03	2.046 -03	1.846 -03	2.000 -04
8000	4.431 -04	1.832 -03	4.722 -04	3.352 -04	1.370 -04
9000	1.172 -04	8.430 -04	1.475 -04	5.967 -05	8.782 -05
10,000	2.964 -05	3.782 -04	5.723 -05	9.198 -06	4.804 -05

TABLE III. Mols of NO and NO$^+$ given by the Exact and Approximate Methods simple mixture was calculated for all of the temperatures and pressures indicated in Table I. The degree of ionization[3] given by the exact method in this calculation agreed with the degree of ionization given by Saha's equation to within the numerical convergence criteria required in the exact method. (See footnote 1 in Appendix A.)

The second method is considered to be approximate because the only source of the ion of a specie is the original specie itself. Also, the presence of other species, either reactant or nonreactant, is not considered. To determine the effect of the presence of other species the equilibrium composition for a mixture consisting of N, NO, NO^+, and e^- was determined by the exact method for the eight temperatures and three pressures. In this mixture N cannot react with the other species. The degree of ionization of NO as determined by these calculations was significantly higher than the degree of ionization calculated for the mixture of NO, NO^+, and e^-. This result would seem to indicate that the presence of other species would increase the degree of ionization of a particular specie. However, as may be seen in Table II, the number of mols of A^+ given by the approximate method is greater than the number given by the exact method which would indicate that the presence of other species reduces the ionization of argon.

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[3] One mol of NO was considered in this simple mixture; thus the number of mols of NO^+ was equal to the degree of ionization.

To determine the possible effect of sources of a specie ion other than the original specie, calculations were made for NO^+ at T = 6000 °K and P = 0.01 atmosphere. Table III shows that the exact method and step one of the approximate method give almost exactly the same number of mols of NO. Using the number of mols of N, N^+, O, and O^+ given for this reduced system by the exact method at 6000 °K and 0.01 atmosphere pressure, it was determined that $N + O^+$ would give 0.004506 mols of NO^+ and $N^+ + O$ would give 0.01363 mols of NO^+. Since this amount of NO^+ is greater than that for the total system (Table III) at these conditions, it would appear that some, or even a major portion, of the NO^+ given by the exact method may be due to sources other than simply ionized NO. Since in the second method the only source of NO^+ is NO, this method must be considered an approximate method.

The comparison of the exact and the approximate methods would not be complete without a comparison of the computing time[4] required by the two methods. For the exact method the average time required to calculate the equilibrium composition at each pressure and temperature was 32.5 seconds with a high of 46 seconds. For step one of the approximate method the average time required was 11.5 seconds

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[4] The computations for this thesis were performed on the IBM 7040 computer at the Virginia Polytechnic Institute Computing Center. The FORTRAN IV programming language was used.

with a high of 18 seconds. The total time required for the calculations of step two of the approximate method was 22 seconds for all 24 pressure and temperature combinations. The average time required by the approximate method to determine the equilibrium composition for each pressure and temperature therefore was 12.5 seconds. Thus, determining the equilibrium composition by the approximate method required less than 40 percent of the computing time of the exact method.

The difference between the average time and the high time required by the computations is due to differences in the initial set of mol numbers. Equilibrium compositions for several temperatures and pressures were calculated in each computer run and the equilibrium composition computed for a pressure and temperature was used as the initial set of mol numbers for the calculation of the equilibrium composition at the subsequent pressure and/or temperature. Overall computational time was thus reduced by about one third.

CONCLUSIONS

Comparison of the two methods for determining the amount of ionization at equilibrium leads to the following conclusions:

1. Saha's equation gives a number of mols of electrons for the mixture which compares well with the number of electrons given by the method of minimization of free energy with ionization included.

2. If the mols of electrons is less than about 0.1 percent of the total number of mols in the mixture, Saha's equation will give a number of mols of electrons less than that given by the minimization of free energy.

3. The use of Saha's equation to determine the ionization of the species in a mixture of gases (when the equilibrium composition has been determined without ionization) is an approximate method which gives more than acceptable accuracy and offers a significant saving in computational time.

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APPENDIX A

The Equations of Minimization

Following the procedure of reference 1, the problem of determining the equilibrium composition of a mixture of ideal gases is equivalent to determining the non-negative set of mol numbers x_i which will minimize the Gibbs free energy of the mixture. For minimization purposes a non-dimensional form of the free energy may be written as

$$F(X) = \sum_{i=1}^{n} f_i \quad , \tag{A-1}$$

where f_i is the non-dimensional free energy of specie i given by

$$f_i = x_i \left(\frac{F^o}{RT} \right)_i + x_i \ln \left(\frac{x_i}{\bar{x}} P \right) \tag{A-2}$$

and

$$\bar{x} = \sum_{i=1}^{n} x_i \tag{A-3}$$

P = the total pressure in atmospheres, and

X = the set of mol numbers $\{x_1, x_2, \ldots x_n\}$.

The above equations define F(X) as a function of n variables, namely, the n mol numbers x_i. The total pressure, P, and the standard Gibbs free energies, F_i^o, are constants for any particular equilibrium determination.

The mol numbers are not independent but must obey constraint relations given by conservation of mass and charge. The constraint equations are

$$\sum_{i=1}^{n} a_{ij} x_i = b_j \quad (j = 1, 2, \ldots, m) \quad , \qquad \text{(A-4)}$$

where there are m atomic components in the mixture. The a_{ij} are the formula numbers giving the number of atoms of component j in a molecule of species i, and b_j is the total number of gram-atoms of component j present in the mixture. Inclusion of ionization in the problem requires that the electrons be treated as a separate component.

For any arbitrary set of positive mol numbers, such as $Y = \{y_1, y_2, \ldots, y_n\}$ the non-dimensional free energy of the mixture is given by

$$F(Y) = \sum_{i=1}^{n} y_i \left[\left(\frac{F^o}{RT} \right)_i + \ln \left(\frac{y_i}{\bar{y}} P \right) \right] \qquad \text{(A-5)}$$

with

$$\bar{y} = \sum_{i=1}^{n} y_i \quad . \qquad \text{(A-6)}$$

Denoting the differences $x_i - y_i$ by Δ_i and $\bar{x} - \bar{y}$ by $\bar{\Delta}$, F(Y) can be expanded in a Taylor's series about Y. Neglecting terms higher than second order gives the quadratic approximation

$$Q(X) = F(Y) + \sum_{i} \frac{\partial F_i}{\partial x_i}\bigg|_{X=Y} \Delta_i$$

$$+ \frac{1}{2} \sum_{i} \sum_{k} \frac{\partial^2 F}{\partial x_i \, \partial x_k}\bigg|_{X=Y} \Delta_i \, \Delta_k \quad . \tag{A-7}$$

From equation (A-2), it can be seen that the partial derivatives of F in equation (A-7) are given by

$$\frac{\partial F(X)}{\partial x_i} = \left(\frac{F^o}{RT} \right)_i + \ln P + \ln \frac{x_i}{\bar{x}} \tag{A-8}$$

and

$$\frac{\partial^2 F(X)}{\partial x_i \, \partial x} = \frac{\delta_{ik}}{x_i} - \frac{1}{\bar{x}} \tag{A-9}$$

where δ_{ik} is the Kronecker delta. Equation (A-7) then becomes

$$Q(X) = F(Y) + \sum_{i} \left[\left(\frac{F^o}{RT} \right)_i + \ln P + \ln \frac{y_i}{\bar{y}} \right] \Delta_i$$

$$+ \frac{1}{2} \sum_{i} y_i \left(\frac{\Delta_i}{y_i} - \frac{\bar{\Delta}}{\bar{y}} \right)^2 \quad . \tag{A-10}$$

Since Q(X) is an approximation to F(X), the minimization of Q(X) would give an approximation of the minimum of F(X). To minimize Q(X) subject to the constraints given in equations (A-4) the method of Lagrange multipliers is used and the function G(X) is defined by

$$G(X) = Q(X) + \sum_{j} \pi_j \left(- \sum_{i} a_{ij} \, x_i + b_j \right) \tag{A-11}$$

where the π_j are the Lagrange multipliers.

The necessary conditions for G(X) to have a minimum are $\frac{\partial G(X)}{\partial x_i} = 0$, which give the n equations

$$\frac{\partial G(X)}{\partial x_i} = \left[\left(\frac{F^o}{RT} \right)_i + \ln P + \ln \frac{y_i}{\bar{y}} \right] + \left[\frac{x_i}{y_i} - \frac{\bar{x}}{\bar{y}} \right] - \sum_i \pi_j a_{ij} = 0 \qquad \text{(A-12)}$$

Equations (A-3), (A-4), and (A-12) provide n + m + 1 linear simultaneous equations in n + m + 1 unknowns; the n mol numbers x_i, the m Lagrange multipliers, and $\bar{x}$. This system of equations may be reduced to m + 1 equations in m + 1 unknowns. Equation (A-12) is rearranged to give x_i explicitly as

$$x_i = - F_i(Y) + \frac{y_i}{\bar{y}} \bar{x} + \left(\sum_{j=1}^{m} \pi_j a_{ij} \right) y_i \qquad \text{(A-13)}$$

where

$$F_i(Y) = y_i \left[\left(\frac{F^o}{RT} \right)_i + \ln P + \ln \frac{y_i}{\bar{y}} \right] . \qquad \text{(A-14)}$$

Equation (A-13) is summed from i = 1 to i = n and gives

$$\sum_{j=1}^{m} \pi_j b_j = \sum_{i=1}^{n} F_i(Y) . \qquad \text{(A-15)}$$

Substitution of equation (A-13) into equation (A-4) gives

$$\sum_{k=1}^{m} r_{ik} \pi_k + b_j u = \sum_{i=1}^{n} a_{ij} F_i(Y) \quad (j = 1, 2, \ldots, m) \qquad \text{(A-16)}$$

where

$$r_{jk} = r_{kj} = \sum_{i=1}^{n} (a_{ij}\, a_{ik})\, y_i \quad (j, k = 1, 2, \ldots, m) \qquad \text{(A-17)}$$

and

$$u = \frac{\bar{x}}{\bar{y}} - 1 \quad . \qquad \text{(A-18)}$$

Equations (A-16) and (A-15) give m + 1 linear equations in m + 1 unknowns; the m π_j's, and u. The values of u and the π_j determined by equations (A-16) and (A-15) are substituted into equation (A-13) to give the values of the x_i, which are the mol numbers that minimize Q(X). If all of the x_i are positive these values may be used as a new set of Y and another computation cycle begun. This procedure is repeated until a computation cycle gives values of x_i which are sufficiently close[1] to the values of x_i given by the previous cycle.

Before replacing Y by X and beginning a new iteration cycle, several checks of the mol numbers need to be made. First, the mol numbers must be positive, but some of the x_i may become negative. To eliminate the possibility of negative mol numbers an adjusted set of mol numbers $X' = \{x_1', x_2', \ldots, x_n'\}$ is determined by

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[1] The convergence criteria set for all species was $|x_i - y_i| < 0.75 \times 10^{-4}$. Also, a second convergence criteria was set: that the values of x_i must be within 0.1 percent of the values of y_i. This criteria does not permit the solution to converge while the mol numbers of the minor species are still being significantly adjusted.

$$x_i' = y_i + \lambda(x_i - y_i) \quad (i = 1, 2, \ldots , n) \tag{A-19}$$

where λ is a fractional multiplier and satisfies the inequality $0 < \lambda \leq 1$. The value of λ chosen is the largest value which will give all x_i' positive. If only one x_i is negative, the value of λ would be slightly less than $y_i/(y_i - x_i)$.

Also, λ is used to determine if the minimum point of F has been passed. The derivative of F(X) is computed from the expression

$$\frac{dF}{d\lambda} = \sum_{i=1}^{n} (x_i - y_i) \left[\frac{F_i^o}{RT} + \ln P \frac{x_i'}{\bar{x}'} \right] , \tag{A-20}$$

where $\bar{x}'$ is given by

$$\bar{x}' = \bar{y} + \lambda\ (\bar{x} - \bar{y}) \quad . \tag{A-21}$$

The value of λ is then chosen small enough so that $dF/d\lambda \leq 0$. The mol numbers given by equation (A-19) using this value of λ are then substituted for Y and used as a starting point for a new iteration cycle.

Before a new iteration cycle is begun, though, some of the mol numbers are adjusted to compensate for round-off errors. The values of b_j $(j = 1, 2, \ldots , m)$ are computed using the new values of Y and compared with the previous values of b_j. Denoting these values by b_j' and b_j respectively, the mol numbers are adjusted by selecting the most abundant species which contain component j (j = 1, 2, ...,m) and replacing the mol numbers of these species by the value of

$$y_i + \frac{b_j - b'_j}{a_{ij}}$$

where y_i is the new value of the mol number.

APPENDIX B

Choice of Energy Reference Levels

When calculating the thermodynamic properties for the different species in a mixture of gases from the quantum-mechanical partition function, the energy levels used in the partition function of each specie are evaluated relative to the ground state of the molecules of that specie. The thermodynamic functions of each specie are thus evaluated relative to the ground state of that specie. In order to calculate the thermodynamic properties of the mixture (e.g., the free energy) it is necessary that the thermodynamic properties of each specie be evaluated relative to a common energy reference level.

In this thesis the thermodynamic property which is used is the Gibbs free energy and the effect of the choice of different reference levels for energy may be readily illustrated. Equation (7) gives

$$F = - N\,kT \ln \frac{Q}{N} \tag{B-1}$$

and the partition function Q is given by

$$Q = \sum_{i} g_i \exp\left(- \frac{\epsilon_i}{kT}\right) \quad . \tag{B-2}$$

In equation (B-2) the energy of the i^{th} energy level is referred to the ground level for that particular specie of molecule. If the ground level of these molecules is at energy ϵ', measured from some other energy level which is chosen to be a new reference level, the partition function, Q', referred to this new energy level is

$$Q' = \sum_i g_i \exp\left(- \frac{\epsilon' + \epsilon_i}{kT}\right) . \qquad \text{(B-3)}$$

This may be rearranged to give

$$Q' = \exp\left(- \frac{\epsilon'}{kT}\right) \sum_i g_i \exp\left(- \frac{\epsilon_i}{kT}\right) .$$

$$= \exp\left(- \frac{\epsilon'}{kT}\right) Q \qquad \text{(B-4a)}$$

or

$$Q = \exp\left(\frac{\epsilon'}{kT}\right) Q' \qquad \text{(B-4b)}$$

The free energy F may then be expressed in terms of Q' by substituting equation (B-4b) into equation (B-1), giving

$$F = - N\, kT \ln \left(\exp\left(\frac{\epsilon'}{kT}\right) \frac{Q'}{N}\right) \qquad \text{(B-5a)}$$

or

$$F = - N \epsilon' - N\, kT \ln \frac{Q'}{N} . \qquad \text{(B-5b)}$$

In terms of the partition function Q', the free energy F' would be

$$F' = F + N \epsilon' = - N\, kT \ln \frac{Q'}{N} . \qquad \text{(B-5c)}$$

If ϵ' in the above development is chosen in such a way that it relates the ground state energy level of the molecules of each specie in the mixture to a common reference level, then the free energy F' of the various species may be properly combined. Since Q is more easily calculated than is Q', equation (B-5c) and equation (B-1) are combined to give

$$F' = N\,\epsilon' - N\,kT\,\ln\frac{Q}{N}\ . \qquad \text{(B-6)}$$

If equation (B-6) is written for one mole of the species at standard pressure, the result is

$$\frac{F^{o'} - E^{o'}}{T} = -\,R\,\ln\left(\frac{Q}{N_o}\right)_{P=1\text{ atm}}, \qquad \text{(B-7)}$$

where $R = N_o k$ and $E^{o'} = N_o\,\epsilon'$. The superscript zero indicates the property for one mole of the species at standard pressure, referred to as the standard molal property. The reference level of energy commonly used in the compilation of thermodynamic tables is the energy of the species at T = 0 °K. For the elements as they naturally occur at standard temperature (T = 25 °C) and standard pressure (P = 1 atm.), for example O_2, H_2, N_2, A, etc., this energy level is assigned the value zero. For other species (e.g., NO and H_2O) the energy at 0 °K is the standard heat of formation of the species, $H_o^{\,o}$. Thus if $E^{o'}$ in equation (B-7) is replaced by $H_o^{\,o}$, $F^{o'}$ is then replaced by $F_T^{\,o}$, the standard molal free energy at temperature T, giving

$$\frac{F_T^{\,o} - H_o^{\,o}}{T} = -\,R\,\ln\left(\frac{Q}{N_o}\right)_{P=1\text{ atm}} \qquad \text{(B-8)}$$

which is the free energy function frequently tabulated. The function needed in the minimization of free energy, $\frac{F_T^{\,o}}{RT}$, may be obtained by rearranging equation (B-8).

APPENDIX C

The Limit for the Summation of the Diatomic Vibration-Rotation Partition Function

In order to determine the termination point for the series in equation (70) it is necessary to have the value of the dissociation energy hc D_o. In reference 11 the dissociation energy is given for the ground state but not for the excited electronic states. Since the internal force field may be different for the excited electronic states than for the ground state, the dissociation energy should also be different.

An approximation of the dissociation energy for each electronic energy level may be obtained from the energy of vibration of the molecule. With j = 0 equation (68) reduces to

$$\epsilon(v,o) = hc\ (v\ (\omega_e - \omega_e \chi_e) - v^2\ \omega_e \chi_e) \quad . \qquad \text{(C-1)}$$

Since $\omega_e \chi_e \ll \omega_e$ it is seen that equation (C-1) has a maximum. If the dissociation energy hc D_o corresponds to this maximum value of the energy of vibration, the dissociation energy is then given by the expression

$$D_o = \frac{(\omega_e - \omega_e \chi_e)^2}{4\ \omega_e\ \chi_e} \quad . \qquad \text{(C-2)}$$

In equation (C-1) the first term corresponds to the energy of the harmonic oscillator with a first correction for anharmonicity. The term in v^2 is a second correction term and terms in v^3 and higher powers of v are available from perturbation theory; however, the spectroscopic constants which are needed for use in terms containing v in powers higher than two are generally unavailable.

The maximum value of the quantum number v is determined by requiring that the energy of the harmonic oscillator given by the first term of equation (C-1) is less than the approximate dissociation energy given by equation (C-2). This requirement is represented by the inequality

$$v(\omega_e - \omega_e \chi_e) \leq \frac{(\omega_e - \omega_e \chi_e)^2}{4\ \omega_e\ \chi_e} \quad . \qquad \text{(C-3)}$$

If the vibration quantum number could have non-integer values, v_{max} would be given by

$$v_{max} = \frac{\omega_e - \omega_e \chi_e}{4\ \omega_e\ \chi_e} \quad . \qquad \text{(C-4)}$$

Since v can have only integer values, v_{max} is the largest integer whose value does not exceed the value given by equation (C-4).

APPENDIX D

Derivation of the Rotation Partition Function

As given in reference 6, the summation over the quantum number j in equation (69) can be reduced to a compact form by using the Euler-Maclaurin summation formula. For a general function with summation index n this formula gives

$$\sum_{n=a}^{\infty} f(n) = \int_{a}^{\infty} f(x)\, dx + \frac{1}{2} f(x)\Big|_{x=a}$$

$$- \frac{1}{12} f'(x)\Big|_{x=a} + \frac{1}{720} f'''(x)\Big|_{x=a} - \frac{1}{30240} f^{V}(x)\Big|_{x=a}$$

$$+ \ldots \qquad . \qquad \text{(D-1)}$$

By rearranging terms equation (69) may be written as

$$Q_{vib,rot} = \frac{1}{\sigma} \sum_{v=o}^{\infty} \exp\left[- vu + v\,(v-1)\, \chi u\right] \cdot$$

$$\cdot \sum_{j=o}^{\infty} (2j + 1) \exp\left[- \beta_o j\,(j+1)(1-j\,(j+1)\, P - vq)\right] \quad \text{(D-2)}$$

where the expressions for u, x, β_o, P, and α are given by equations (71).

The summation over j in equation (D-2) is related to equation (D-1) by the expression

$$\sum_{j=o}^{\infty} f(j) = \sum_{j=o}^{\infty} (2j + 1) \exp \left[-j(j + 1)(1 - j(j + 1)\ P - vq)\ \beta_o \right] . \tag{D-3}$$

The first derivative of f(j) may be easily obtained and f and f' evaluated at j = o give

$$f(j) \Big|_{j=o} = 1 \tag{D-4a}$$

$$f'(j) \Big|_{j=o} = 2 - \beta_o\ (1 - vq)\ . \tag{D-4b}$$

The higher order terms were not retained in reference 6 and since succeeding terms should decrease rapidly the terms in f''', f^v, etc. may be omitted.

The first term of equation (D-1) is given by

$$\int_o^{\infty} f(j)dj = \int_o^{\infty} (2j+1)\ \exp \left[-\ \beta_o j\ (j+1)(1-j\ (j+1)\ P\ -\ vq) \right] dj\ . \tag{D-5}$$

By the substitution Z = j(j+1) equation (D-5) may be simplified to

$$\int_o^{\infty} f(j)\ dj = \int_o^{\infty} \exp\ (-\ \beta_o Z + \beta_o\ P\ Z^2 + \beta_o\ v\ qZ)\ dZ$$

or

$$\int_o^{\infty} f(j)\ dj = \int_o^{\infty} e^{-\beta_o(1-vq)Z}\ e^{\beta_o P\ Z^2}\ dZ\ . \tag{D-6}$$

In the derivation of equation (D-6) the only approximations that have been made were for the energy of vibration and rotation and the summation formula. Just as the summation of j in equation (69) was nonconvergent, the integrand of equation (D-6) above is not bounded as Z increases without limit. The series was evaluated by terminating the series and an equivalent result can be obtained for equation (D-6). As in reference 6 the integral is evaluated by expanding exp (β_o P Z^2) in a Maclaurin series and retaining only the first two terms. According to reference 6 this procedure introduces only slight error into the value of the partition function. This procedure results in the expression

$$\int_o^\infty f(j)\,dj = \frac{1}{\beta_o(1-vq)} \int_o^\infty (1 + \frac{P\,y^2}{\beta_o(1-vq)^2})\ \exp\,(-y)\,dy \qquad (D-7)$$

where $y = \beta_o(1-vq)\ Z$.

Equation (D-7) is evaluated by the gamma function integral giving

$$\int_o^\infty f(j)dj = \frac{1}{\beta_o(1-vq)}\ (1 + \frac{2P}{\beta_o(1-vq)^2})$$

or

$$\int_o^\infty f(j)\,dj = \frac{1}{\beta_o(1-vq)} + \frac{2P}{\beta_o^2(1-vq)^3}\ . \qquad (D-8)$$

Substitution of equations (D-4) and (D-8) into equation (D-1) gives the result

$$\sum_{j=o}^{\infty} f(j) = \frac{1}{\beta_o(1-vq)} + \frac{2P}{\beta_o^{2}(1-vq)^{3}} + \frac{1}{2} - \frac{1}{12}(2-\beta_o\,(1-vq))$$

$$+ \text{ terms of higher order.} \qquad \text{(D-9)}$$

Substitution of equation (D-9) into equation (D-2) gives the partition function of rotation and vibration for each electronic energy level as

$$Q_{vib,rot} = \frac{1}{\sigma} \sum_{v=o}^{v_{max}} \left[\frac{1}{\beta_o(1-vq)} + \frac{2P}{\beta_o^{2}(1-vq)^{3}} + \frac{1}{3} \right.$$

$$\left. + \frac{\beta_o(1-vq)}{12} \right] \exp\left[- vu + v(v-1)\,\chi u \right]. \qquad \text{(D-10)}$$

In developing equation (D-10) fewer approximations were made and fewer terms were neglected than were in reference 6 in the development of the high temperature correction terms. As a result the partition function given by equation (D-10) should be more accurate than the rigid rotator - harmonic oscillator partition function with closed form high temperature correction terms added which is the final result of the development in reference 6.

The development of the partition function given in equation (D-10) imposes an additional restriction on the maximum value of the vibration quantum number. For the integral in equation (D-7) to exist the argument of the exponential term must be negative. This requires that $y = \beta_o(1-vq)Z > 0$. Since β_o and Z are always positive the condition for the existence of the integral is

$$1 > vq = v \frac{\alpha_e}{B_e - \frac{1}{2}\alpha_e} \quad .$$

Rearranging this inequality gives

$$v < \frac{B_e - \frac{1}{2}\alpha_e}{\alpha_e} \quad .$$

This inequality was obeyed by all of the values of v_{max} calculated by the procedure of Appendix C except for the $C^2\ \Sigma^+$ state of N_2^+. For this exception the value of v_{max} was chosen to be the largest integer value of v which satisfied the inequality above.

APPENDIX E

Atomic and Molecular Thermodynamic Constants and Fundamental Constants of Physics

The atomic and molecular constants which were used in calculating the molal standard free energy are given in Table IV below. The sources of the constants are given following the table.

TABLE IV

Atomic and Molecular Constants

Specie	Symmetry Number, σ	Molecular Weight (grams/mol)	Heat of Formation (ergs/mol)
e^-	---	5.4876×10^{-4}	---
H	---	1.00813	2.16031×10^{12}
H^+	---	1.00760	1.528502×10^{13}
C	---	12.00386	7.11569×10^{12}
C^+	---	12.00331	1.799059×10^{13}
C^{++}	---	12.00276	4.152369×10^{13}
N	---	14.00754	4.70834×10^{12}
N^+	---	14.00699	1.875034×10^{13}
N^{++}	---	14.00644	4.733394×10^{13}
O	---	16.00000	2.45166×10^{12}
O^+	---	15.99945	1.559526×10^{13}
O^{++}	---	15.99890	4.952626×10^{13}

(Continued)

TABLE IV (concluded)

Specie	Symmetry Number, σ	Molecular Weight (grams/mol)	Heat of Formation (ergs/mol)
A	---	39.9756	0.0
A^+	---	39.9753	1.52106×10^{13}
A^{++}	---	39.9745	4.18742×10^{13}
H2	2	2.016	0.0
C2	2	24.022	8.21712×10^{12}
N2	2	28.016	0.0
$N2^+$	2	28.016	1.504055×10^{13}
02	2	32.000	0.0
02^+	2	32.000	1.163365×10^{13}
02^-	2	32.000	-9.6278×10^{11}
OH	1	17.008	4.1327×10^{11}
OH^+	1	17.008	1.349917×10^{12}
CO	1	28.011	-1.13868×10^{12}
CO^+	1	28.011	1.23896×10^{13}
NO	1	30.008	8.9903×10^{11}
NO^+	1	30.008	9.8721×10^{12}
CN	1	26.019	4.56274×10^{12}
C02	2	44.004	-3.93335×10^{12}

The molecular weights of the atomic species are from page 450 of reference 16. The molecular weights of the diatomic species and CO_2 are from reference 13 except for the species H_2, OH, and OH^+. For H_2, OH, and OH^+ the molecular weight was obtained from the atomic weights of the components.

The heat of formation of the molecular species is from reference 13 except for OH and OH^+ for which the heat of formation was derived from the ground state dissociation energy given in reference 11. The heat of formation of C is from reference 17 and the heat of formation of H, N, and O was determined from the dissociation energy of H_2, N_2, and O_2 given in reference 11. The heat of formation of the atomic ions was derived from the ionization potential given in reference 18 except the heat of formation of H^+ was derived from the ionization potential of H given in reference 19.

The constants of physics and conversion factors which were used in the calculations are given in Table V.

TABLE V

Constants of Physics and Conversion Factors

From reference 19:

the velocity of light

$c = 2.99793 \times 10^{10}$ cm/sec

Avagadro's number

$N_o = 6.02486 \times 10^{23}$ particles/mol

Planck's Constant

$h = 6.62517 \times 10^{-27}$ erg sec

Boltzmann Constant

$k = 1.38044 \times 10^{-16}$ erg/deg

and the conversion factor

$1 \text{ ev} = 1.60206 \times 10^{-12}$ erg

From reference 16:

$P^o = 1 \text{ atm} = 1.01325 \times 10^6$ dyne/cm

and

$1 \text{ kcal} = 4.186 \times 10^{10}$ erg .

APPENDIX F

Atomic and Molecular Spectroscopic Constants and Energy Levels

The energy levels used to calculate the internal partition function of the atomic species were from reference 18. All of the energy levels listed in reference 18 were used up to the ionization limit except the energy levels for those terms with principal quantum number greater than six. If all of the energy levels given in reference 18 had been included individually in the internal partition function the computing time would have been excessive. Effective energy levels were formed by taking the arithmetical average of a group of closely spaced energy levels and adding the degeneracies for each individual energy level. The energy levels for such groups were within about one percent. As an example, for three energy levels with energies of 135,000 cm^{-1}, 135,400 cm^{-1} and 136,000 cm^{-1} and degeneracies of 3, 5, and 3 respectively, the effective energy level would be 135,500 cm^{-1} with a degeneracy of 11. Differences in the value of the partition function due to using combined energy levels instead of using all energy levels individually should not occur except at temperatures considerably higher than those considered.

The electronic energy levels and spectroscopic constants for those energy levels for the molecular species, except for the species C_2, CN, H_2, OH and OH^+, were from reference 13. The electronic energy levels and spectroscopic constants for C_2 and CN were from reference 15. Except for the values of $\omega_e\chi_e$ for)H^+, the electronic energy levels and spectroscopic constants for H_2, OH and OH^+ were from reference 11. The values of $\omega_e\chi_e$ for OH^+ were calculated using the relation given in reference 11,

$$\alpha_e = \frac{6\,B_e^{\,2}}{\omega_e}\left[\left(\frac{\omega_e\,\chi_e}{B_e}\right)^{1/2} - 1\right]$$

which can be rearranged to give $\omega_e\chi_e$ in terms of B_e, α_e, and ω_e as

$$\omega_e\,\chi_e = B_e\left[\frac{\alpha_e\,\omega_e}{6\,B_e^{\,2}} + 1\right]^2 .$$

A COMPARISON OF TWO METHODS FOR DETERMINING THE IONIZATION IN A MIXTURE OF IDEAL GASES AT EQUILIBRIUM

by

Earnest Wade Miner

ABSTRACT

Two methods of determining the ionization in a mixture of ideal gases at equilibrium are compared. The equilibrium composition for a mixture of 1000 grams of air, with 10 grams of added water vapor, is determined by minimizing the Gibbs free energy of the mixture of gases. The Gibbs free energy of each specie in the mixture was computed using the partition function of statistical thermodynamics. Ionization is included in determining the equilibrium composition by the first method; in the second method, however, the equilibrium composition is calculated with no ions included. Ionization is then determined in the second method by calculating the degree of ionization from the Saha equation (using the equilibrium constant formulation) for each individual specie in the mixture. The results given by the two methods are compared for temperatures of 3000° to 10,000° Kelvin in 1000° increments, with pressures of 0.01, 1.0, and 10 atmospheres considered at each temperature. The results compare favorably

throughout these temperature and pressure ranges. The results also show that computing time is reduced by more than sixty percent when the ionization is determined using the Saha equation.